ELECTRICAL ENGINEERING RESEARCH LABORATORY
ENGINEERING EXPERIMENT STATION
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

STATUS REPORT
ON
RESEARCH ON THE ELECTRICAL PROPERTIES
OF
SEMI-CONDUCTORS

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31 May 1953

Approved by:

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1. INTRODUCTION

1.1 Purpose

This is the third status report on the lead telluride investigation being carried out under ONR sponsorship at the University of Illinois, and covers the period 1 February 1953 to 31 May 1953. The purpose of the investigation is to study the semi-conductor properties of PbTe single crystals of various compositions. The first major phase of the undertaking was to produce single crystal samples. This has finally been accomplished with a successful run which yielded a single crystal 1 1/8" in length by ½" in diameter.

1.2 Personnel

There have been no changes in personnel since the last status report. During the spring semester, Mr. Sirrine devoted full time to the project and Prof. Murrell one-quarter time. Because of a special series of courses on semiconductors and transistor electronics being offered this summer at the University of Illinois, only one month will be free for research before the fall semester. At that time it is hoped to add another graduate student to the project.

2. EQUIPMENT AND FACILITIES

No major additions in general equipment or facilities have been made. A number of revisions of existing apparatus have been made and will be described below.

3. SUMMARY OF ACTIVITIES

3.1 Tellurium Purification

The tellurium sublimation apparatus was improved by replacing all rubber stoppers with ground glass joints. The procedure was altered by adding a preliminary step. Tellurium is loaded into the boat, brought to the melting point and held there for 30 minutes in an atmosphere of specially purified hydrogen. Helium is then substituted for hydrogen and the regular fractional sublimation process carried out. A spectroscopic analysis of the tellurium purified in this manner (after two sublimations) showed less than 0.001% lead as the only detectable impurity.

3.2 Mixing Process

The apparatus used for mixing the constituents is made of Pyrex, except for the portion to be sealed off and used as the crucible, which is joined to the rest of the apparatus through a graded seal. Heaters are wound around the Pyrex to control the temperature of the various parts. One step in the process is heating the lead in a hydrogen stream for some time to remove the oxide. A small amount of residual oxide seems to remain even after prolonged heating, so the Pyrex will be replaced by Vycor to permit the temperature to be raised to 600°C.

Fused quartz is now being used instead of Vycor for the crucible. Although this increases the difficulties of the sealing-off step, the change may have contributed to the success of the crystal growing attempts, so its use will be continued.

3.3 Crystal Growing

Three modifications were made in the Stockbarger-Bridgman furnace. The rate of lowering the sample was increased from 1/16 inch per hour to 3/16 inch per hour, and the temperature gradient was increased from 100°C per inch to 150°C per inch. To ensure that the entire length of the crucible would be held above the PbTe melting point, the windings in the upper half of the furnace were revised to provide a longer section of uniform temperature.

A number of the earlier runs resulted in the crucible's cracking at some time during the cooling down period. In all cases there was obvious oxidation of the boule, especially in the neighborhood of the crack. An annealing procedure has overcome this difficulty. After the crucible has passed entirely through the gradient, it is held at 800°C for 30 hours or more and then brought down to room temperature over an eight hour period.

All the modifications described in this and in the previous two sections were made just prior to the last of a series of ten runs. After being lowered through the gradient, the sample was annealed for 40 hours. The resulting boule was 1 1/8" in length by ½" in diameter.

The original constituents were made up with a slight excess of Pb. As expected, the top of the boule, the last part to solidify, was covered with a cap of free Pb. For such a sample, grain boundaries would be expected to contain free Pb. The boule was etched with a solution of 0.02 N NaOH in 30% H_2O_2, which is designed to attack Pb. The only evidence of etching action was in the free Pb at the top.

Next, a flat surface along the boule was ground, highly polished, and again etched. Once more there was no evidence of grain boundaries. Sandblasting the polished surface brought out a series of parallel elongated indentations, indicating an oriented crystal formation throughout the sample. The boule was readily cleaved along planes perpendicular to the indentation lines.

3.4 Electrical Measurements

Wafers cleaved from both ends of the single crystal boule were checked with a thermoelectric probe. Those from the lower end were all p-type, while those from the top near the excluded free Pb were n-type. Room temperature measurement of the rectification effect confirmed this. Both types of samples were placed in a cold chamber micromanipulator and investigated at liquid nitrogen temperature. In general, the rectification was found to improve at the lower temperature. A first attempt to observe transistor action was not successful.

A few measurements of resistivity have indicated the need for something better than pressure contacts for the current leads. Consequently, a method of plating nickel onto the PbTe is being worked on. One sample has been successfully plated and nickel wires soldered to the ends. Measurements of the resistivity were 2.7×10^{-2} ohm-cm at room temperature and 1.1×10^{-8} ohm-cm at liquid nitrogen.

4. PLANS FOR THE NEXT INTERVAL

In the series of ten runs made so far, some contained slight excess Pb and others, slight excess Te. In both cases, the excess material is largely excluded during growth and appears at the top of the boule. This experience has led us to reconsider the original plan of controlling the semi-conductor properties by measured departures from stoichiometric proportions. It might be more fruitful to carry the process toward higher purity and more regular crystal orientation and then develop a doping procedure. To do this, zone purification has been considered and will probably be tried eventually.

In a recent conversation during a visit to our laboratory, Walter Brattain suggested that doping by a substitutional alloying process be considered. The problem is being studied, with the substitution of trivalent La for Pb as a possible approach.

Some further purification of the lead seems possible, as indicated in Section 3.2. This will be carried out, and a systematic series of conductivity and Hall mobility measurements will be started using n- and p-type cleaved samples as they occur. If the alloying process shows promise, it might be possible to produce samples with more systematically controlled properties and with longer life minority carriers. In this event, drift mobility measurements would become possible.

With the limited amount of time available during the summer months, only a portion of the above can be undertaken before the next status report.

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